A PROCESS FOR DRY HYDROGENATION OF LOW RANK COALS WITH HIGH YIELDS OF PHENOLICS

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INTRODUCTION

The available methods for converting coal into gaseous or liquid fuels or chemicals are generally forms or combinations of three basic processes. These are pyrolysis or carbonization, hydrogenation, and $CO-H_2$ synthesis gas production with further conversion of the synthesis gas if desired. The doubtful economics and precarious existence of the forms which these basic processes have taken stem from several factors. Low-temperature carbonization produces a crude tar product in low yield and must be coordinated with a power-plant requiring the residual coke or char. High-pressure hydrogenation, as in the commercialized German Bergius process, is technologically difficult, requires heavy investment per barrel of crude product, and consumes large amounts of expensive hydrogen from synthesis gas. The handling of the pulverized coal as a slurry in heavy re-cycle "pasting" oil is a complicating feature. The various $CO-H_2$ syntheses, such as the Fischer-Tropsch process, require high investment in both synthesis gas production and the synthesis step itself.

In seeking a more economically attractive route to products from coal, we have studied the pyrolysis of coals under mildly hydrogenating conditions in the absence of a liquid vehicle; i.e., in a fluidized bed of solid particles of coal and reacted char. We looked for coals that gave attractive yields of tar by carbonization, we investigated regions of low hydrogen consumption to minimize the cost and we accepted an incomplete conversion of coal substance to gas and liquid product with the char by-product treated as the basic fuel for plant operation. As a chemical company we were seeking chemical rather than energy products and were particularly interested in the potentially high phenolic yields obtainable from low-rank coals.

Dry hydrogenation of coal was investigated briefly and apparently abortively in Germany during World War II[1]. The U.S. Bureau of Mines[2] followed up this work immediately after the war and coined the term hydrocarbonization which we use in this report. The Bureau describes their effort to develop a process by hydrocarbonization as an alternate to the Bergius process for the production of liquid fuels from coal. However, there seems to have been no major effort at exploitation of this work at any later time.

The work reported here is primarily based on a bench-scale experimental effort (about one pound of coal per hour) carried out several years ago mainly with a Wyoming, subbituminous C coal from Lake de Smet. Two scale-ups were also successfully operated, at about 10 and about 1500 pounds per hour. Each of these scale-ups produced its own operating problems. But in each case these were surmounted and operability and yields equivalent to those from the bench-scale operation were achieved. Several other coal feeds were studied. Wyoming (subbituminous C) from Wyodak, Texas Lignite, and North Dakota Lignite were essentially equivalent to Lake de Smet coal. Elkol and Brilliant Wyoming coals and weathered Pittsburgh No. 8 were less satisfactory but could be handled.

EXPERIMENTAL

Apparatus (Bench-Scale Unit)

The bench-scale hydrocarbonization unit as it finally evolved is shown in Figure 1. Its nominal capacity is 1.0 lb/hr of 40-100 mesh coal.

The system consists of the following major items:

Coal Feed Hopper - sized to hold about 3500 grams of coal, enough for 6-10 hours operation. Constructed from schedule 80, 3-inch carbon-steel pipe, 4 feet high.

Calibrated Thermal-Feed Rate Device - a miniature heat exchanger to indicate a rough coal feed rate.

Calibrated Vibratory Coal Feeder - based on a chicken-feeder principle for gas flow to pick up a controlled amount of coal.

Fluidized Reactor - stainless steel, 1-inch I.D., 1/4-inch wall thickness, 9 inches high with expanded head 18 inches high made of 2-inch schedule 80 pipe. Char overflow line and vapor outlet made from 1-inch schedule 80 pipe. A 1/4-inch thermowell is installed in the center of the reactor. Thermocouples are located one inch, four inches, seven inches and twelve inches from the bottom of the reactor. The lower three thermocouples are in the fluidized carbonization bed while the upper one is in the vapor space above the bed. The reactor is equipped with four independent electrical heating circuits, one each for the reactor, the expanded head, the vapor outlet line, and the char overflow line.

Char Receiver - a duplicate of the coal feed hopper.

Steam-Cooled Primary Condenser - stainless steel, 1-1/2-inch, schedule 80, 22 inches long with a 2-inch steam jacket.

Water-Cooled Condenser - carbon steel, 1-inch, schedule 40, 44 inches high with a 1-1/2-inch jacket.

Ice-Water-Cooled Condenser - duplicate of water-cooled condenser.

Operating, Sampling, and Analytical Procedures

The feed coal was removed from a vacuum drier at ambient temperature and a weighed sample was charged to the feed hopper. Meanwhile, fine adjustments of the current to the electrical heating elements brought the various parts of the unit to the target temperatures. The unit was pressurized and gas flows at target conditions were established. The run was then started by opening the shut-off valve in the line separating the feed hopper from the coal feeder and starting the Syntron vibrator which was attached to the coal feeder body. Prior to starting the coal-feed, the current to the electrical heating element on the thermal feed-rate device had been adjusted to a level such that the thermocouple indicated a temperature of 140°C. After establishing coal flow, the cold coal flowing through the tube from the hopper to the feeder conducted heat away from the metal core of the feed-rate device and the thermocouple temperature lined out at a lower level. Calibration of the feeder, prior to experimental runs, showed that a temperature level of about 100°C. would result in a coal feed rate of about one pound per hour, the desired rate for the majority of the experiments. The amplitude of vibration to the feeder was, therefore, varied to adjust the temperature to the 100°C. level. The feeder device works on the principle of a "chicken feeder"; i.e., the gas flowing across the supply of coal in the enlarged part of the body below the cut-off tubing eats away the coal which is continuously replaced by coal from the hopper. The function of the vibrator is to ruffle the coal interface so that more coal will be picked up as the amplitude of vibration is increased.

The vibrations also insure that the down-tube from the coal hopper remains full. Minor feed-rate adjustments of about 50 grams on a base of 450 grams per hour could be achieved by changing the amplitude of vibration. During the run, the quality of fluidization was monitored by the temperature spread in the bed as indicated by a spread, top to bottom, of about 10°C. It was desirable to have good fluidization with the minimum of fluidizing gas in order to minimize char carryover. Therefore, the gas flow to the unit was generally reduced to a point where a slight temperature spread in the bed developed, then the flow was increased in small increments until the spread disappeared. To achieve equilibrium at target operating conditions required about 10 minutes.

A composite gas sample was collected at a constant rate by liquid displacement throughout the run. Spot gas samples were also taken.

Normally, with minor adjustments, the runs proceeded until the coal feed-hopper was empty. This point was rapidly indicated by a sudden increase in the temperature of the thermal feed-rate device. With the termination of the experiment, the unit was closed in at pressure, gas flows stopped, electric circuits turned off and the unit was allowed to cool overnight.

The char receiver was drained and the char weighed to determine the char yield. It was found that the char ignited spontaneously at room temperature in an open container. It was therefore stored in a drum pressurized with nitrogen.

The condensers were drained into a common receiver jar and a net liquid gross product weight was determined. The entire liquid product was then filtered and charged to a 1-inch I.D. by 20-inch-high glass distillation column packed with 1/4-inch protruded packing. The char filter cake weight was determined after it was dry and this weight, between 15 and 30 grams, was added to the char yield.

The product was then stripped of water by distilling at atmospheric pressure and on total make to a kettle temperature of 200°C. Some oil azeotroped with the water and was subsequently separated by decantation and returned to the kettle after it cooled. The tar was then cut into four fractions as follows:

(1) IBP to 130°C. at atmospheric pressure and a 3 to 1 reflux ratio.

(2) 130-260°C. light oil, at 50 mm and a 6 to 1 reflux ratio.

(3) 260-340°C. middle oil, at 10 mm and a 3 to 1 reflux ratio, and

(4) Residue, boiling >340°C. and consisting of the heavy oil and pitch. In some runs the heavy oil (340-350°C. at 10 mm) and pitch fractions were determined by a Vigreux distillation.

The analyses performed on the various samples, for the most part, are standard or well-known and it is not necessary to document them here. However, there was one special analytical development during the course of the experiments, i.e., the determination of the concentration of various tar acids boiling through the xylenols, without separation from the neutral oil, by a gas chromatographic technique. This method of determining at least a partial distribution of phenolics in raw light oils from coal carbonization, etc., can be extremely useful in following effects of changes in processing. With a column packed with Chromosorb coated with Apiezon N stopcock grease, or with similar neutral columns, the order of elution is: Phenol; o-cresol; m-p-cresols; o-ethylphenol; 2,5-xylenol; 2,4-xylenol; 2,3-xylenol, m-p-ethylphenol; 3,5-xylenol; and 3,4-xylenol. 2,6-Xylenol is eluted somewhere between m-p-cresol and o-ethylphenol, and m-p-ethylphenol about the same time as 2,3-xylenol. M- and p-cresol are unresolved, and the nine ethylphenols and xylenols give at most six incompletely resolved peaks,

some of which may also contain small amounts of C_3-phenols. Nevertheless, considerable information concerning a sample may be obtained by this simple form of chromatography, certainly enough to follow substantial changes in distribution. Interference from hydrocarbons present is corrected for by a comparison with the chromatograph of a typical neutral oil, prepared by extraction of product oil with caustic.

Protection of Coal from Oxidation

In the preliminary experiments with Lake de Smet coal, an important lesson on handling the coal was learned. It was found that extreme care was necessary in order to prevent oxidation and obtain truly representative yields from this low-rank coal. The precautions decided upon as a result of the preliminary work were used in succeeding experiments with Lake de Smet coal.

A sample of Lake de Smet coal was obtained by core-drilling south of the lake on property of the Northern Wyoming Land Company. The sample of coal was carefully protected for shipment by placing the wet cores in polyethylene bags and surrounding the bags with wet core-cuttings in a wooden packing box. On arrival at the research laboratory, an aliquot sample of the cores was taken, partially dried at ambient temperature in a vacuum desiccator, ground and analyzed. The remaining core samples were placed in a commercial vacuum drying oven and dried overnight at 50°C. The cores were then ground to yield sufficient 40-100 mesh coal for two experimental runs.

The analysis of the aliquot sample, the sample prepared for experimental use and an analysis reported by the United States Bureau of Mines, Denver, Colorado, are shown in Table I. The operating conditions and the product yields are shown in Table II.

The yield of tar from the experimental supply of Lake de Smet coal was only 5.9% MAF coal when carbonized in an inert atmosphere as shown in Column 1, Table II. This compares with a 10.9% yield reported by the U.S.B.M., shown in Column 4. The respective char yields were 76.6% and 68.4%. Furthermore, Column 2 shows that in a hydrogen atmosphere, at a hydrogen partial pressure of 320 psi, the tar yield increased to only 8.9%. We had anticipated a tar yield of about 17% as shown in Column 3. The respective char yields were 68.9 and 57.0%. Turning to the ultimate analyses given in Table I, it is apparent that the experimental supply of coal lost hydrogen, down from 5.3 to 4.3% and gained oxygen, up from 19.1 to 20.3% during the drying and grinding operations. The adverse effect of oxidation on the tar yields from these preliminary experiments shows that extreme care is required in handling the coal in order to obtain truly representative yields.

After this experience the following procedure was used to prevent oxidation of the feed coal. The Lake de Smet coal was received from Wyoming in drums with the coal completely submerged in water. As needed for a series of experiments, lumps of coal were removed from the water and placed in the vacuum dryer. The coal was dried initially to a moisture level between 20 and 25%, the drying-time required being determined by trial and error. (The coal as mined has a 30% moisture content). The vessel and the partly dried coal were then allowed to cool to ambient temperature prior to breaking the vacuum and removing the coal. The partly-dried coal was ground and screened to obtain a maximum yield of coal in the range of 40-100 mesh. This was the size of coal used throughout the experiments. The minus 100 mesh was rejected in order to minimize char carryover with the vapors from the fluid bed into the condensers. Between runs, the partly dried ground coal was stored in sealed drums under positive pressure supplied by high-purity nitrogen cylinders.

The day before a run was to be made, sufficient coal for making the run (about 4000 grams) was removed from the nitrogen-pressurized drum and charged to the vacuum oven for final drying at 50°C. About 6 hours were required to reduce the moisture content from 20-25% to about 1-3%. The oven was allowed to cool before the coal was removed.

EXPERIMENTAL RESULTS

The experimental results presented in this paper are all based upon Lake de Smet, Wyoming, coal. This unusual coal formation exists in the form of a lens of coal lying near the surface and with thickness up to 200 feet. At some time in the past the coal has partially burned out, forming a basin now filled with water and known as Lake de Smet. The coal is of subbituminous C rank, with a heating value of about 7,000 B.t.u. per pound as mined. Because the thickness of the seam and the relatively modest overburden make for low-cost mining, the deposit is a potential cheap source of raw material.

A typical analysis of Lake de Smet coal is:

Ultimate Analysis , Wt. % on Moisture-free and Ash-free Basis

C	72.0
H	5.5
N	1.4
S	1.1
O (by difference)	20.0
Ash, dry basis	17.0

North Dakota and Texas lignites, and Wyodak, another Wyoming subbituminous C coal, have similar analyses and give almost identical results.

Comparison of Hydrocarbonization with Carbonization

It is clear from the data presented, and the comparison given with carbonization in nitrogen, that hydrocarbonization differs substantially and quantitatively from carbonization. There is considerable reaction with hydrogen, the yield of tar is roughly doubled, the proportions of light oil and of -230°C. phenols in the tar are increased. The following short table summarizes the main differences. Before any experimentation on Lake de Smet coal, yields of tar from hydrocarbonization were predicted from the Bureau of Mines carbonization data with factors estimated from German and Bureau work on dry coal hydrogenation. At 1000 psi, 525°C. and 8 minutes coal residence time a tar yield of about 25% was predicted. Coal residence time is defined as the time required to fill the reactor with fresh coal feed.

Yields as Wt. % MAF Coal	Carbonization in N_2 This Work	Carbonization By Parry Process USBM Data[3]	Hydrocarbonization This Work 1.6% H_2 Reacted
Char	67	67	49
Tar	12	12	25
Gas	9	8	14
Water	12	13	14
<260°C., Light Oil	4	3	10
<230°C., Phenols	2	1.5	5.2
Phenol	0.5	0.5	1.9

A decided advantage of hydrocarbonization is the possibility of recycling products, especially phenolics, to the reactor and reducing their molecular weight to the range desired - to phenol if necessary. Even in a straight carbonization plant enough facility and hydrogen would probably have to be supplied to carry out this hydrocracking step.

Effects of Operating Variables

Effect of Temperature
Operating temperatures of 478 to 567°C. were studied with hydrogen

partial pressure and coal residence time held approximately constant at 900 psia and 9 minutes, respectively. Figure 2 shows the dependence of hydrogen consumption on the temperature variable and Figure 3 shows the yields. Figure 4 shows that at temperatures much above 520°C. rapid increase in hydrogen consumption does not result in significant increases in tar yield. Actually the curve drawn in Figure 3 indicates a maximum tar yield at about 540°C.

Effect of Hydrogen Partial Pressure
The partial pressure of hydrogen was varied in the range 0 to 940 psia with temperature and coal residence time held at about 540°C. and 8 minutes, respectively. Figure 5 indicates a roughly linear dependence of hydrogen consumption on partial pressure. Figure 6 shows that tar rises proportionately. A single experiment at 1500 psi indicated that the yield of tar is still an increasing function of pressure above 1000 psi.

Effect of Coal Residence Time
Figure 7 shows the effect of coal residence time at constant temperature and hydrogen partial pressure (about 900 psia). The shape of the curves we have drawn, at low residence times, is roughly that of a typical first-order reaction. Rate constants can be estimated by assuming each curve approaches some maximum hydrogen consumption. This is shown for 540°C. where 3.5% hydrogen consumed is arbitrarily called "complete reaction." Figure 8 shows product yields at 540°C. as a function of residence time. At this temperature there is little or no gain in tar yield after about 8 minutes, although hydrogen consumption continues to rise.

Effect of Ash and Water
Batches of Lake de Smet coal from two sections of the area had quite different ash contents. The results plotted in Figure 9 show that the low ash sample was slightly less reactive, perhaps indicating some catalytic activity in the ash.

Batches of Lake de Smet coal dried to various water contents were also studied, but no differences noted.

Composition of Gas, Tar, and Char Products
Gas: Table III shows typical gas product analyses under mild and severe hydrocarbonization conditions. In both cases the B.t.u. content is high and there are potential chemical values.

Tar: Table III also gives typical analyses for tars from the same experiments. Our particular interest is in the phenolics content and distribution. The tar acid distribution seems to be fairly insensitive to the severity of hydrogenation and there is a surprisingly high content of phenol itself.

Char: The ultimate analyses of the chars for the runs are given in Table III. There is still some oxygen in the char at the higher severity, although other experiments have shown this to approach zero at slightly higher temperatures or longer residence times. There is about 4% hydrogen in both chars. In general we have found the hydrogen content to be relatively independent of operating conditions.

Hydrocarbonization Under Mild Conditions
Studies under very mild hydrocarbonization conditions showed that a high percentage of the tar and phenolic value could be recovered with very low hydrogen consumption at a hydrogen partial pressure of about 300 psi. For example a 5.1% light oil tar acid yield was obtained with only 1.4% hydrogen consumption. The yield of phenol was 1.8%. This compares to a light oil tar acid yield, at 900 psi hydrogen partial pressure, of 5.7% of MAF coal. However, the hydrogen consumption was 2.2% and the phenol yield was 1.6% MAF coal. Since a major cost factor in the process is the consumption of hydrogen per unit of phenolics produced, a mild condition of hydrocarbonization is probably economically desirable.

TABLE I

PROPERTIES OF LAKE DE SMET COAL

Proximate Analysis, Wt. %	Aliquot Sample as Received	Experimental Sample	Denver Station, USBM, Run 146
Volatile Matter	33.8	38.2	28.2
Fixed Carbon	35.8	45.9	30.9
Moisture	19.3	1.5	24.8
Ash	11.1	14.4	16.1
Ultimate Analysis, Wt. % MAF Coal			
C	72.4	72.2	70.2
H	5.3	4.3	5.5
N	1.6	1.5	1.5
S	1.6	1.7	0.7
O (by difference)	19.1	20.3	22.1

TABLE II

CARBONIZATION AND HYDROCARBONIZATION
OF LAKE DE SMET COAL

Operating Conditions

			Estimate*	U.S.B.M. Denver Station, Run 146
Fluidization Gas	Nitrogen	Hydrogen	Hydrogen	Nitrogen
Pressure, psig	200	400	400	Atmospheric
Temperature, °C.	515	515	515	500
Hydrogen Partial Pressure, psi	nil	320	320	nil

Yield, Weight % MAF Coal

Char	76.6	68.9	57.0	68.4
Tar	5.9	8.9	17.0	10.9
Gas	9.0	11.6	15.0	8.4
Water	8.5	11.5	12.0	12.3
Hydrogen	-	-0.9	-1.0	-
	100.0	100.0	100.0	100.0

* Estimated by interpolation of German and USBM data on low-rank coals.

TABLE III

COMPOSITION OF GAS, TAR, AND CHAR

Operating Conditions

Hydrocarbonization	Mild	Severe
Temperature, °C.	560	567
Hydrogen Partial Pressure, psi	310	940
Residence Time, Minutes	8.2	10.2

Yields, Weight % MAF Coal

	Mild	Severe
Char	50.4	38.4
Tar	21.3	29.0
Water	13.2	19.2
Gas	16.0	16.2
Hydrogen	-1.4	-3.5
Unaccounted for	0.5	0.7
	100.0	100.0

Gas Composition, Volume %, H_2 Free

Component	Mild	Severe
Methane	46.3	63.1
Ethane	9.1	13.7
Propylene	1.8	0.3
Propane	4.7	4.5
Butenes	1.1	0.6
n-Butane	0.4	0.5
i-Butane	0.7	0.4
C_5's	0.2	0.1
CO	28.2	14.1
CO_2	7.5	2.5
H_2S	0.2	0.2
Molecular Weight	25.5	22.36
Wt. % Hydrogen in Gas	12.1	17.34

Tar Composition

Distillation, Weight % of Tar

Fraction, From-to, °C.	Mild	Severe
IBP-260°C.	37.0	44.5
260-340°C.	12.0	7.0
340°C.	51.0	48.5

Tar Acids, Weight % MAF Coal

	Mild	Severe
IBP-260°C.	5.1	7.6
260-340°C.	1.5	0.8

Yield of Basic Aromatics, Lb/Ton MAF Coal

	Mild	Severe
Benzene	0.1	0.4
Toluene	0.2	0.2
Naphthalene	0.3	0.6

TABLE III, CONTINUED

COMPOSITION OF GAS, TAR, AND CHAR

Tar Composition, Continued

Hydrocarbonization	Mild	Severe
Light Oil (130-260°C.) Tar Acid Distribution, Wt. %		
Phenol	34.5	33.4
o-Cresol	8.7	7.8
m,p-Cresol	27.2	24.5
Ethylphenols and Xylenols	17.1	18.9
Higher Phenols by Difference	12.5	15.4
Phenol Yield, Weight % MAF Coal		
	1.8	2.2
Char Composition		
C	90.1	93.0
H	3.9	3.8
N	1.2	1.3
S	1.0	0.6
O (by difference)	3.8	1.3

Oil Recycle Experiments

The hydrocarbonization of Lake de Smet coal produces considerable tar boiling above 230°C. As a general rule, about 50% or more of the tar falls in this category. Tar acid content of the +230°C. tar is roughly 50 weight %. Experiments on both bench- and pilot-plant scales have shown that this oil can be recycled to extinction in the reactor, thus converting the heavy tars to oils boiling below 230°C.

The bench-scale unit was modified by the addition of a heated pump, so that the hydrocarbonization tar boiling above 230°C. could be fed into a fluidized bed of char produced from previous hydrocarbonization experiments. The results of these experiments show that the conversion of +230°C. tar acids to -230°C. phenolics was about 40% by weight. Thus the yield from recycling +230°C. tar is 40% of 50% or about 20 weight % of the total +230°C. tar cycled. The consumption of hydrogen per pound of -230°C. phenolics produced is about half that for phenolics from raw Lake de Smet coal. Therefore, it should be feasible and economical to recycle these higher-boiling tars to the basic hydrocarbonization process.

DISCUSSIONS AND CONCLUSIONS

Chemistry

Coals of lignitic or subbituminous rank are statistically polymers of fairly small aromatic "nuclei" averaging perhaps 10 aromatic carbon atoms per nucleus. These are substituted with paraffin side-chains, probably largely methyl, saturated rings, hydroxyl and other groups and are linked and perhaps cross-linked through hetero-atoms or by direct C-C bonding. The pyrolytic break-down of these crude polymers produces fragments averaging much higher hydrogen content than the coal. Thus, a large amount of a material of low hydrogen content, char or coke, must be produced. When molecular hydrogen is present this can intervene to supply some of the H requirement of the hydrogen-rich fragments, thus reducing the amount of char formed and increasing tar and gas yields.

We would expect the hydrogen action to be roughly first-order in unreacted coal substance (if such a thing is definable) and, by analogy to the well-known thermal dealkylation reaction, half-order in H_2. The activation energy of the reaction should correspond to that of hydrodealkylation or of thermal cracking and be in the 50-60 kcal/mol range.

In practice this very simplistic view of the kinetics of the process is helpful in rationalizing the results but is hardly very satisfactory quantitatively. If we pick a suitable percentage of hydrogen as complete reaction (say 3.5 lbs H_2/100 lbs MAF coal), we can roughly reproduce the general shape of the plots of hydrogen reacted vs coal residence time as a first-order plot (see Figure 7). However, the rate of hydrogen conversion depends upon the first or even higher power of the hydrogen partial pressure (see Figure 5) and the temperature coefficient is low (we estimate the energy of activation to be about 33 kcals/mole).

If we think of degree of reaction strictly in terms of hydrogen consumption per 100 pounds of coal, we can deduce a convenient rule of thumb from the collected data. Doubling the coal residence time is equivalent to doubling the hydrogen partial pressure and either is equivalent to a 25°C. increase in reaction temperature.

The relative rate of desirable and undesirable competitive reactions is extremely important in setting the reactor design and operating conditions. The vapor residence time must be such as to allow a high degree of conversion of the recycled high-boiling tars without serious destruction of the valuable 180-230°C. phenolics. Methanation of carbon monoxide, and other reactions which use up hydrogen non-productively should be minimized, while conditions favoring supplemental production of hydrogen by the shift reaction are desirable. These problems of setting optimum conditions were among those studied on the pilot-plant scale and it is believed that reasonable solutions are found.

It is of interest to follow the oxygen balance from coal substance to products. Under optimum mild hydrogenation conditions the following is typical.

Oxygen in Product Named, lbs/100 lbs MAF Coal

180-230°C. Phenolics	0.7
+230°C. Tar	1.1
Char	2.0
Gas (Carbon Oxides)	3.2
Water	14.0
Total in Coal Feed	21.0

Clearly, most of the coal oxygen is converted to water and the percentage convertible to useful phenolics is small. Direct determination of OH in subbituminous and lignite coals shows as much as 8% phenolic oxygen, but evidently most of this us-unstable to pyrolysis or hydrogenation. Nevertheless, the 0.7 pound of oxygen in the 180-230°C. phenolics represents about 90 pounds of phenolics per ton of MAF coal with perhaps another 50 or 60 pounds obtainable by recycle of the +230°C. tars. Our data indicate a total hydrogen consumption of less than two pounds per hundred pounds of MAF coal to achieve this yield.

Economics
The economics of any coal conversion process is so strongly tied to the cost of mining, transportation, cooling water, etc., and to the marketing problems that it is futile to generalize. The authors believe that the dry hydrogenation process worked out by Union Carbide will, at corresponding scales and under particular, realistically possible, raw material and marketing conditions, look economically good in comparison with any of the known variations of the conversion reactions -- to chemicals or fuels -- discussed in the introduction.

LITERATURE CITED

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(2) Report of Investigations 4456, Part I, Oil from Coal - Synthetic Liquid Fuels - 1948 Annual Report of the Secretary of the Interior (1949).
(3) Landers, W. S., Parry, V. F., Gomez, M., Wagner, E.O., Goodman, J. B., and Nelson, C. R., Carbonizing Properties of Wyoming Coals, U. S. Bureau of Mines, Report of Investigations 5731, (1961).
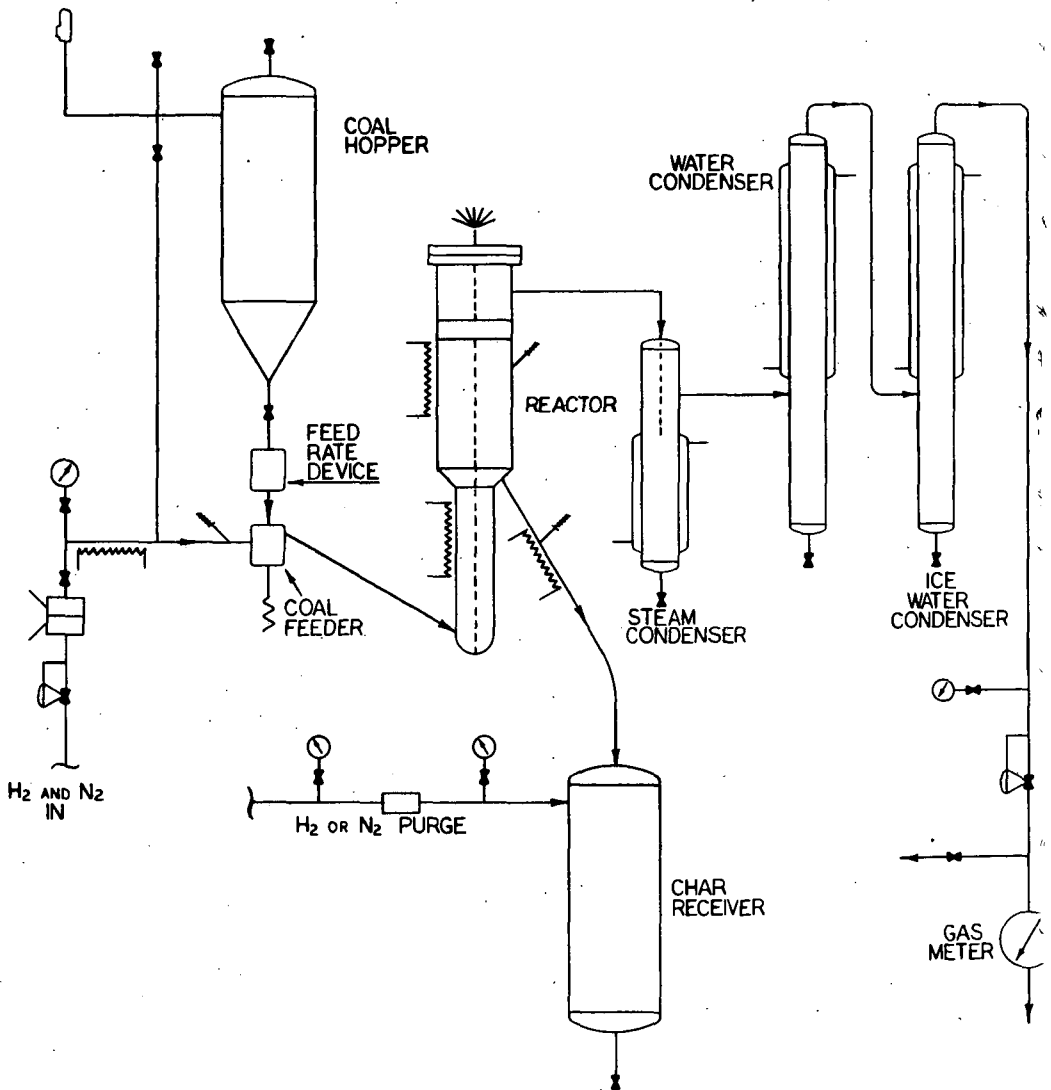
HYDROCARBONIZATION UNIT

COAL
HOPPER

WATER
CONDENSER

REACTOR

FEED
RATE
DEVICE

COAL
FEEDER

STEAM
CONDENSER

ICE
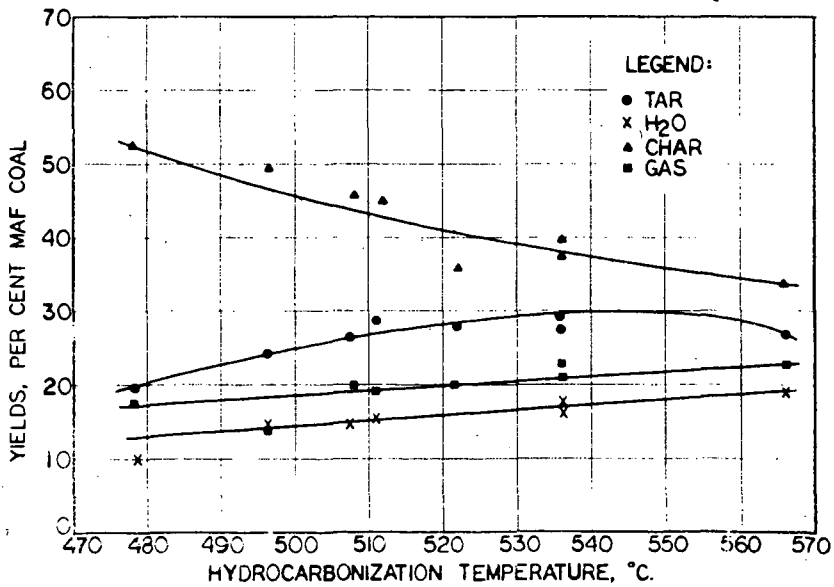WATER
CONDENSER

H₂ AND N₂
IN

H₂ OR N₂ PURGE

CHAR
RECEIVER

GAS
METER

FIG. I

HYDROGEN CONSUMED AS A FUNCTION OF TEMPERATURE

COAL RESIDENCE TIME ABOUT NINE MINUTES
HYDROGEN PARTIAL PRESSURE ABOUT 950 psi

HYDROCARBONIZATION TEMPERATURE, °C.
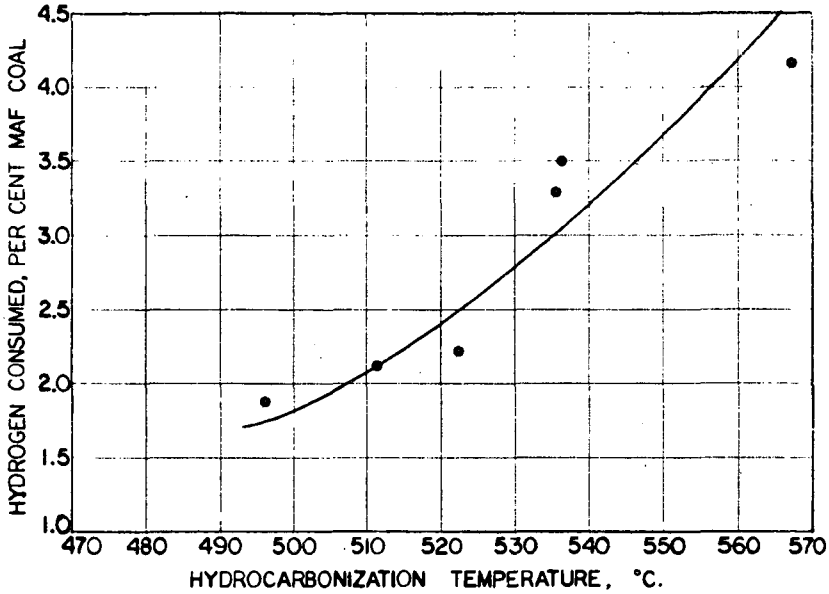
FIG. 2

PRODUCT YIELDS AS A FUNCTION OF TEMPERATURE

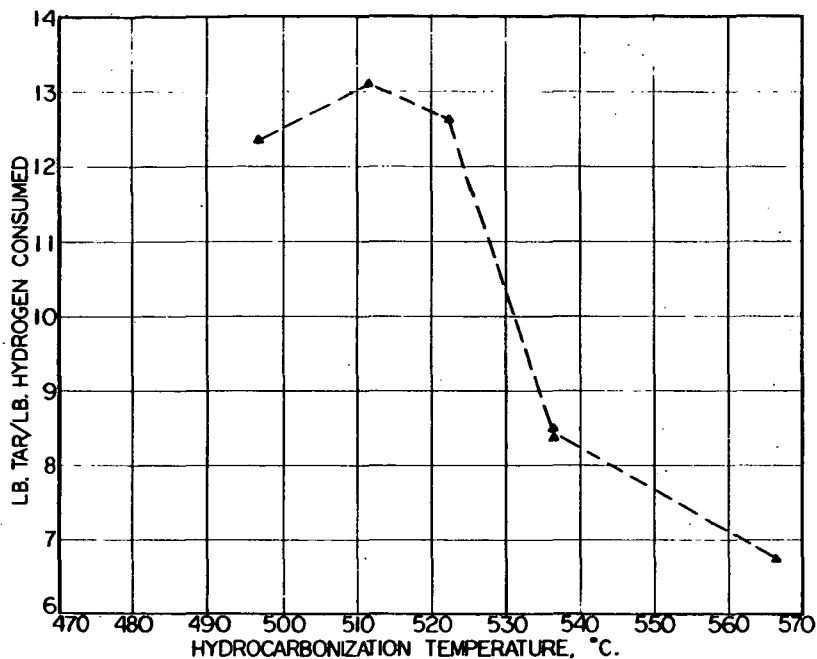COAL RESIDENCE TIME ABOUT NINE MINUTES
HYDROGEN PARTIAL PRESSURE ABOUT 950 psi

LEGEND:
● TAR
× H₂O
▲ CHAR
■ GAS

HYDROCARBONIZATION TEMPERATURE, °C.

FIG. 3

POUNDS OF TAR PER POUND OF HYDROGEN AS A FUNCTION OF TEMPERATURE

COAL RESIDENCE TIME ABOUT NINE MINUTES
HYDROGEN PARTIAL PRESSURE ABOUT 950 PSI

FIG. 4

HYDROGEN CONSUMED AS A FUNCTION OF HYDROGEN PARTIAL PRESSURE

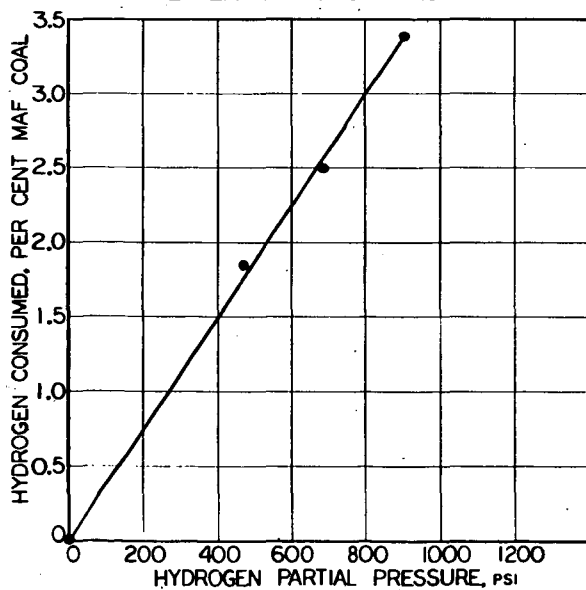COAL RESIDENCE TIME ABOUT NINE MINUTES
TEMPERATURE ABOUT 540 °C

FIG. 5

PRODUCT YIELDS AS A FUNCTION OF HYDROGEN PARTIAL PRESSURE

COAL RESIDENCE TIME ABOUT NINE MINUTES
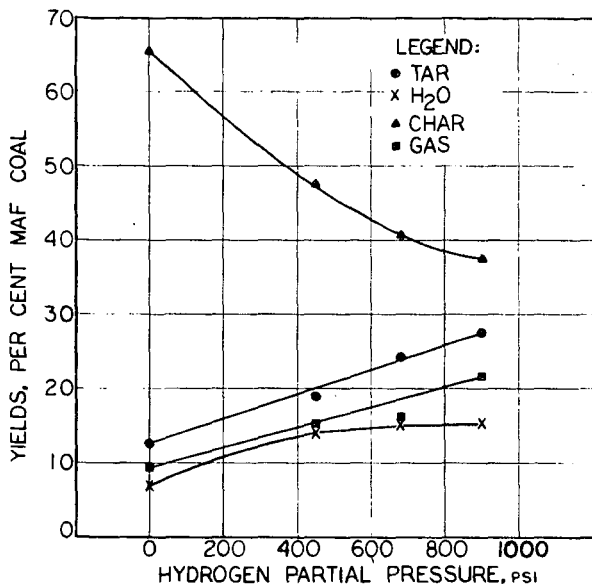TEMPERATURE ABOUT 540 °C

FIG.6

HYDROGEN CONSUMED AS A FUNCTION OF COAL RESIDENCE TIME AND TEMPERATURE
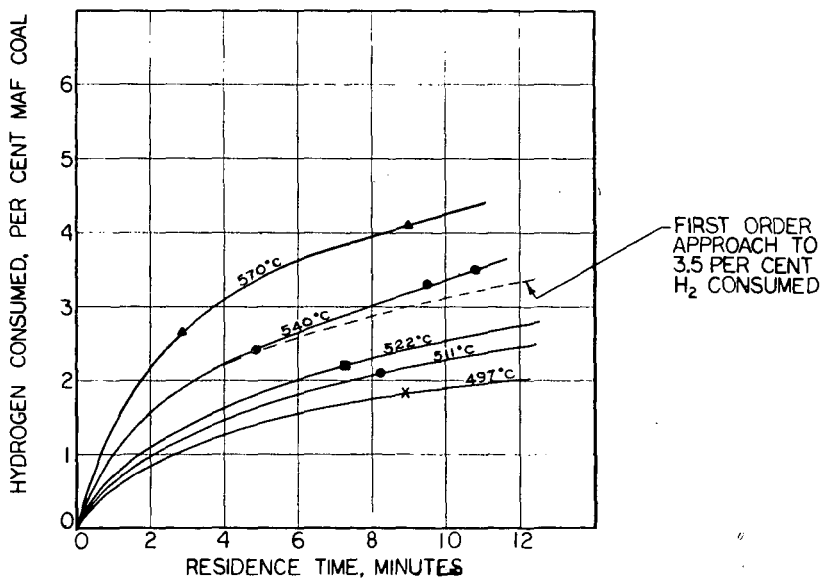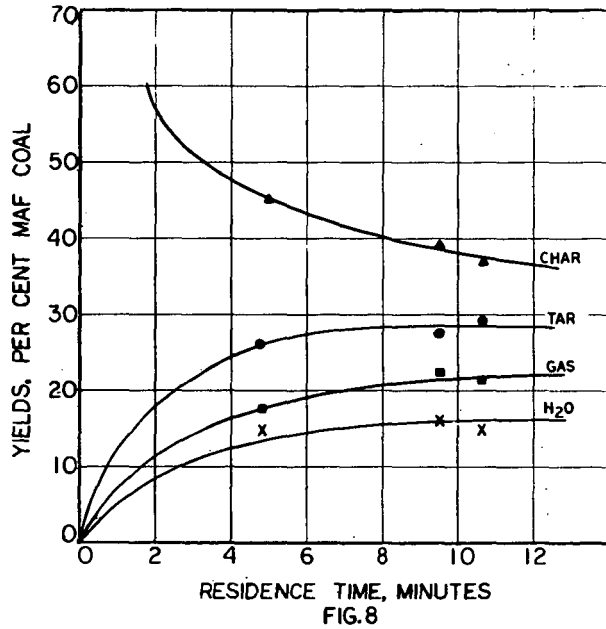
HYDROGEN PARTIAL PRESSURE ABOUT 950 PSI

FIG. 7

PRODUCT YIELDS AS A FUNCTION OF COAL RESIDENCE TIME AT 540 °C

HYDROGEN PARTIAL PRESSURE ABOUT 950 PSI

FIG. 8

PRODUCT YIELDS OF LOW ASH VERSUS HIGH ASH COAL

COAL RESIDENCE TIME ABOUT NINE MINUTES
HYDROGEN PARTIAL PRESSURE ABOUT 950 PSI

FIG. 9